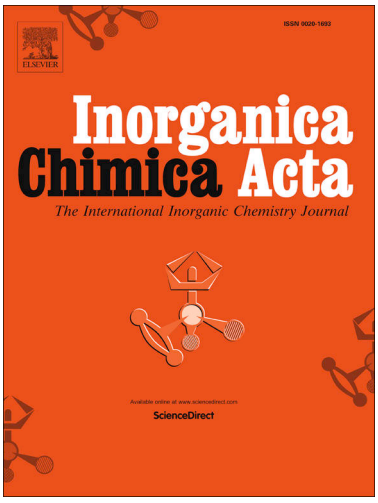
Journal Pre-proofs



Research paper

Synthesis of ferrocenyl imidazolium salts and their novel PEPPSI-type N-heterocyclic Carbene (NHC) palladium complexes

Betül Yenisarı, Rukiye Fırıncı, Namık Özdemir, M. Emin Günay

PII: S0020-1693(20)30991-9
DOI: https://doi.org/10.1016/j.ica.2020.119792
Reference: ICA 119792

To appear in: *Inorganica Chimica Acta*

Received Date: 6 March 2020
Revised Date: 28 May 2020
Accepted Date: 28 May 2020

Please cite this article as: B. Yenisarı, R. Fırıncı, N. Özdemir, M.E. Günay, Synthesis of ferrocenyl imidazolium salts and their novel PEPPSI-type N-heterocyclic Carbene (NHC) palladium complexes, *Inorganica Chimica Acta* (2020), doi: https://doi.org/10.1016/j.ica.2020.119792

Synthesis of Ferrocenyl Imidazolium Salts and their Novel PEPPSI-type N-heterocyclic Carbene (NHC) Palladium Complexes

Betül Yenisarı,[a] Rukiye Fırıncı,[a] Namık Özdemir,[b] M. Emin Günay[a]*

[a]*Department of Chemistry, Faculty of Art and Science, Aydın Adnan Menderes University, 09100 Aydın, Turkey*

[b]*Department of Mathematics and Science Education, Faculty of Education, Ondokuz Mayıs University, 55139 Samsun, Turkey*

***Corresponding author**

E-mail address: megunay@adu.edu.tr (M. Emin Günay)

ABSTRACT

The novel PEPPSI-type palladium complexes of ferrocenyl-functionalized N-heterocyclic carbenes (NHCs) with different substituents were synthesized. The synthesis of these ferrocenyl-NHCs ligands involves the reaction of the alcohol 1-(ferrocenyl)ethanol successively with 1-substituted imidazole in glacial acetic acid. Following that, the novel PEPPSI-type NHC palladium complexes were prepared by heating their imidazolium salts with $PdCl_2$, K_2CO_3 in neat pyridine. In addition, deprotonation of N-ferrocenylethyl-N'-(2,4,6-trimethylphenyl)imidazolium chloride (**2a**) and then its reaction with S_8 gave imidazole-2-thione (**5**). All ligand precursors and all palladium complexes were characterized by elemental analysis, ^1H and ^{13}C NMR, and X-ray diffraction methods for two examples.

Keywords: N-heterocyclic carbene, ferrocenyl-imidazolium salts, PEPPSI-type NHC palladium complexes, X-ray crystallography

1. Introduction

N-Heterocyclic carbenes (NHCs) and their metal complexes have been the subject of extensive investigations owing to their successful applications in coordination chemistry and homogeneous catalysis [1,2]. NHCs have several characteristics, which make them valuable for catalysis. Often, they lead to air-stable compounds, in which the carbene ligands bind more strongly to the metal than in comparable electron-rich phosphine/metal complexes. The strong σ-donor and

comparatively weak π-acceptor properties of NHCs sustain similarities to the coordination characteristics of phosphines, and NHCs are in general more electron-donating than phosphines. Ferrocenyl substituted NHCs have attracted interest because the ferrocenyl group has unique electronic properties, and has an unusual cylindrical shape, and additional electron donation to adjacent electron-deficient centers [3,4]. A number of NHC transition metal complexes bearing ferrocenyl substituents have been synthesized and used in homogeneous catalysis or electrochemical investigation in recent years [5]. The ferrocenyl groups are introduced to the NHCs roughly through two manners, as pendant substituents attached to the side-arm of NHCs [6-9], or as an integral part of the NHC backbone [10,11]. These ferrocenyl functionalized NHCs and their derivatives exhibit spectacular reactivities [12,13] and electrochemical properties [10] owing to the introduction of redox-active ferrocenyl groups. An additional advantage of the ferrocenyl functionalization is that the catalytic activity and selectivity of complexes can be effectively tuned by the redox-active moieties. Thus, NHCs with ferrocenyl substituents are expected to act as very useful ligands for transition metals. In particular, the reason for the synthesis of PEPPSI-type Pd(II)-NHC complexes is that such complexes have great potential in the catalyst for organic transformations such as C-C bond formation and there are a few reports related to especially ferrocenyl bearing PEPPSI-type Pd(II) complexes in the literature.

Herein, the synthesis and characterization of various ferrocenyl NHC palladium(II) complexes were carried out successfully via the deprotonation of the ferrocenyl imidazolium salt by a base followed by subsequent complexation by the palladium center. The compounds were characterized by NMR, elemental analyses, and crystal structures of compounds **4** and **5** were obtained.

2. Experimental

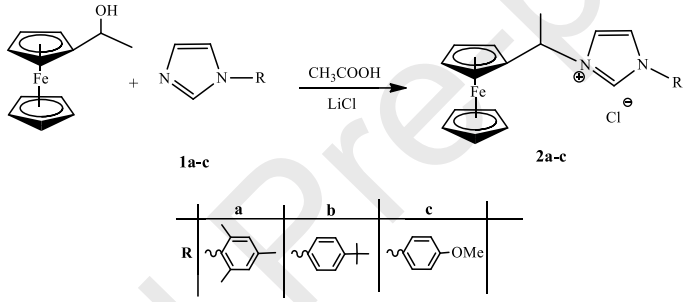
2.1. Materials and general methods

All manipulations except workup and purification were conducted under an inert atmosphere of Ar using standard Schlenk techniques. Solvents were dried and freshly distilled prior to use. All other chemicals were used as received. Acetyl ferrocene [3a,14], ferrocenyl ethanol [15], benzyl bromide derivatives [16], and N-(aryl)-1*H*-imidazole [17] were prepared according to literature procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury AS 400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts are given in ppm with internal

referencing to the solvent peaks. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus. Elemental analyses were performed by the TÜBİTAK (Ankara, Turkey) Microlab.

2.2. Preparation of the imidazolium salts with ferrocenyl substituents, 2a-c.

1-Ferrocenylethanol (1.0 mmol) and *N*-substituted imidazole derivatives (**1a-c**, 1.1 mmol) were dissolved in acetic acid (3.0 mL) and stirred at 60 °C for 7 h (Scheme 1). After removed most of acetic acid, a solution of LiCl (4.0 mmol) in MeOH (20.0 mL) was added, and stirred for 24 h at room temperature. After stirring for 24 h, the volatiles were removed under reduced pressure, and residue extracted with CH_2Cl_2. The solution was filtered through Celite. Removal of solvent under reduced pressure resulted in a liquid. As a result, all the salts synthesized (**2a-c**) were obtained as oily.



Scheme 1. Synthesis of imidazolium salts with ferrocenyl substituents

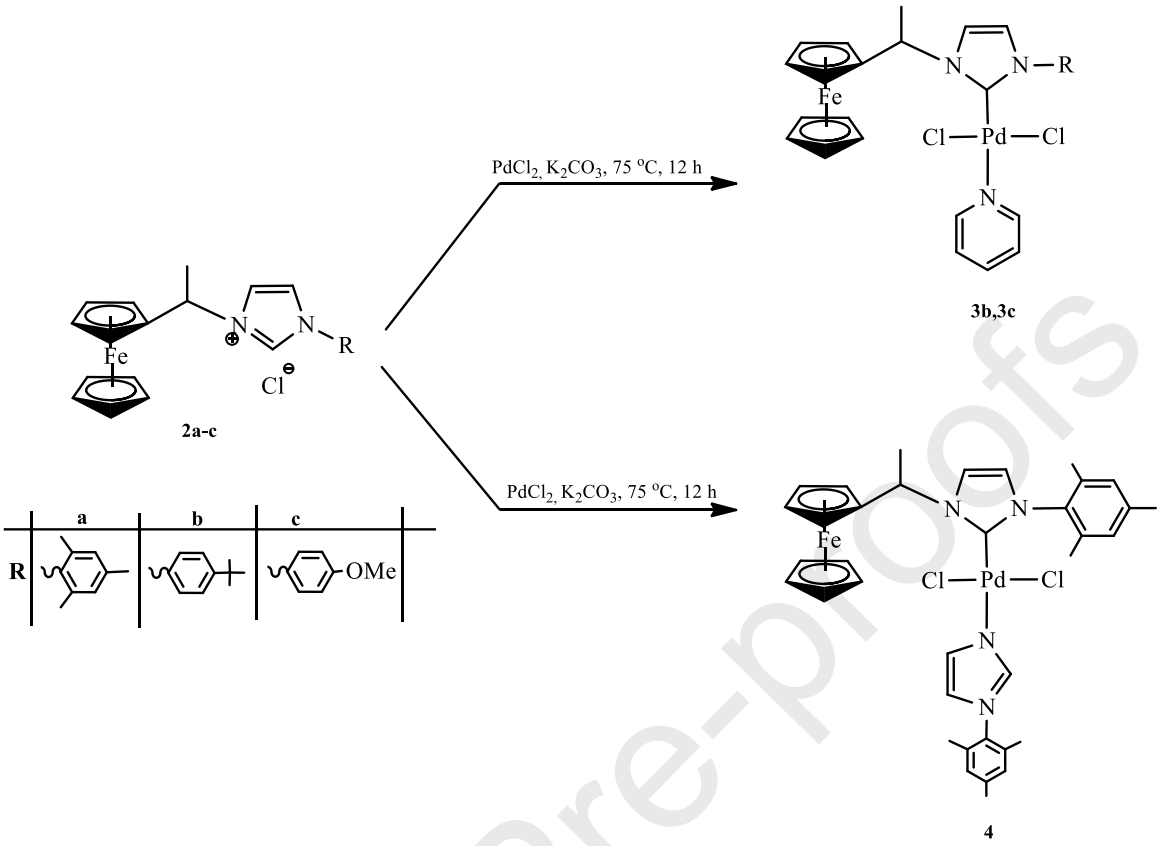
2a: This compound was synthesized according to the literature procedure [18]. Yield: 62% (0.27 g). *Anal*. Calc. for $C_{24}H_{27}ClFeN_2$ (MW = 434.78 g.mol^{-1}): C, 66.30; H, 6.26; N, 6.44. Found: C, 66.41; H, 6.31; N, 6.48%. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, ppm): δ = 1.89 (d, *J* = 7.0 Hz, 3H, FcCHC*H*$_3$), 1.97 (s, 6H, $C_6H_2(CH_3)_3$-*o*-(C*H*$_3$)), 2.30 (s, 3H, $C_6H_2(CH_3)_3$-*p*-(C*H*$_3$)), 4.23 (s, 5H, Fc-*H*), 4.39 (s, 2H, Fc-*H*), 4.44 (s, 2H, Fc-*H*), 5.67-5.82 (m, 1H, FcC*H*CH$_3$), 7.11 (d, *J* = 7.0 Hz, 2H, $C_6H_2(CH_3)_3$), 7.92 (s, 1H, NC*H*CHN), 8.18 (s, 1H, NCHC*H*N), 9.87 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, DMSO-d_6, TMS, ppm): δ = 16.9 (FcCH*C*H$_3$), 20.1 ($C_6H_2(CH_3)_3$), 20.5 ($C_6H_2(CH_3)_3$), 21.1 ($C_6H_2(CH_3)_3$), 55.8 (Fc*C*HCH$_3$), 65.9 (Fc-*C*), 67.3 (Fc-*C*), 68.1 (Fc-*C*), 68.6 (Fc-*C*), 68.8 (Fc-*C*), 78.8 (Fc-*C*), 79.1 (Fc-*C*), 79.4 (Fc-*C*), 87.3 (Fc-*C*), 121.4 (N*C*HCHN), 123.9 (NCH*C*HN), 128.9 ($C_6H_2(CH_3)_3$), 129.1 (($C_6H_2(CH_3)_3$), 131.1 ($C_6H_2(CH_3)_3$), 134.0 ($C_6H_2(CH_3)_3$), 134.4 ($C_6H_2(CH_3)_3$), 136.3 ($C_6H_2(CH_3)_3$), 140.0 (N*C*HN).

2b: Yield: 60% (1.07 g). *Anal*. Calc. for $C_{25}H_{29}ClFeN_2$ (MW = 448.80 g.mol^{-1}): C, 66.90; H, 6.51; N, 6.24. Found: C, 66.68; H, 6.73; N, 6.54%. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, ppm): δ = 1.30 (s, 9H, $C_6H_4C(CH_3)_3$), 1.95 (d, J = 7.0 Hz, 3H, FcCHCH_3), 4.22 (s, 5H, Fc-*H*), 4.47 (s, 2H, Fc-*H*), 4.53 (s, 2H, Fc-*H*), 5.67-5.74 (m, 1H, FcC*H*CH$_3$), 7.61 (d, J = 8.2 Hz, 2H, $C_6H_4C(CH_3)_3$), 7.74 (d, J = 8.6 Hz, 2H, $C_6H_4C(CH_3)_3$), 8.10 (s, 1H, NC*H*CHN), 8.31 (s, 1H, NCHC*H*N), 10.24 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, DMSO-d_6, TMS, ppm): δ = 19.9 (FcCH*C*H$_3$), 30.9 ($C_6H_4C(CH_3)_3$), 34.5 ($C_6H_4C(CH_3)_3$), 55.9 (Fc*C*HCH$_3$), 66.2 (Fc-*C*), 67.9 (Fc-*C*), 68.2 (Fc-*C*), 68.6 (Fc-*C*), 68.8 (Fc-*C*), 78.7 (Fc-*C*), 79.1 (Fc-*C*), 79.4 (Fc-*C*), 87.0 (Fc-*C*), 121.2 (N*C*HCHN), 121.3 (NCH*C*HN), 121.4 ($C_6H_4C(CH_3)_3$), 126.7 ($C_6H_4C(CH_3)_3$), 132.3 ($C_6H_4C(CH_3)_3$), 133.9 ($C_6H_4C(CH_3)_3$), 152.4 (N*C*HN).

2c: Yield: 58% (1.60 g). *Anal*. Calc. for $C_{22}H_{23}ClFeN_2O$ (MW = 422.72 g.mol^{-1}): C, 62.51; H, 5.48; N, 6.63. Found: C, 62.65; H, 5.55; N, 6.76%. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, ppm): δ = 1.94 (d, J = 7.0 Hz, 3H, FcCHCH_3), 3.81 (s, 3H, C_6H_4-*p*-(OCH_3)), 4.22 (s, 5H, Fc-*H*), 4.45 (s, 2H, Fc-*H*), 4.51 (s, 2H, Fc-*H*), 5.62-5.71 (m, 1H, FcC*H*CH$_3$), 7.14 (d, J = 8.0 Hz, 2H, $C_6H_4(OCH_3)$), 7.73 (d, J = 8.0 Hz, 2H, $C_6H_4(OCH_3)$), 8.04 (s, 1H, NC*H*CHN), 8.22 (s, 1H, NCHC*H*N), 10.05 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, DMSO-d_6, TMS, ppm): δ = 19.9 (FcCH*C*H$_3$), 55.6 (C_6H_4-p-(O*C*H$_3$)), 56.0 (Fc*C*HCH$_3$), 66.1 (Fc-*C*), 67.9 (Fc-*C*), 68.8 (Fc-*C*), 68.9 (Fc-*C*), 78.7 (Fc-*C*), 79.0 (Fc-*C*), 79.2 (Fc-*C*), 79.4 (Fc-*C*), 86.9 (Fc-*C*), 114.9 ($C_6H_4(CH_3)$), 121.3 (N*C*HCHN), 123.3 (NCH*C*HN), 127.4 ($C_6H_4(CH_3)$), 127.6 ($C_6H_4(CH_3)$), 127.7 ($C_6H_4(CH_3)$), 127.8 ($C_6H_4(CH_3)$), 159.8 (N*C*HN).

2.3. Preparation of the ferrocenyl NHC-Palladium complexes.

A Schlenk flask was charged with imidazolium salts (**2**, 0.7 mmol), K_2CO_3 (5 mmol), $PdCl_2$ (0.7 mmol), and 5 mL of pyridine (Scheme 2). The reaction mixture was heated with vigorous stirring for 12 h at 75 ^{0}C. The reaction mixture was diluted with CH_2Cl_2 then filtered through a pad of celite and silica gel to remove the unreacted $PdCl_2$ and imidazolium salt. The solvent was removed under vacuum. The obtained yellow solid was recrystallized from CH_2Cl_2/Et_2O.



Scheme 2. Synthesis of ferrocenyl NHC-Pd(II) complexes

3b: Yield: 65% (0.30 g). m.p.: 170-171 °C. *Anal*. Calc. for $C_{30}H_{33}Cl_2FeN_3Pd$ (MW = 668.77 g.mol^{-1}): C, 53.88; H, 4.97; N, 6.28. Found: C, 53.72; H, 4.90; N, 6.42%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ = 1.36 (s, 9H, $C_6H_4C(CH_3)_3$), 1.99 (d, *J* = 6.7 Hz, 3H, FcCHCH_3), 4.07-4.12 (m, 1H, Fc-*H*), 4.21 (d, *J* = 8.6 Hz, 1H, Fc-*H*),4.27 (s, 5H, Fc-*H*), 4.41 (s, 1H, Fc-*H*), 4.72 (s, 1H, Fc-*H*), 6.81 (s, 1H, NC*H*CHN), 6.87-6.92 (m, 1H, FcC*H*CH_3), 7.0 (s, 1H, NCHC*H*N), 7.30-7.33 (d, *J* = 8.0 Hz, 1H, C_5H_5N), 7.53 (d, *J* = 7.8 Hz, 2H, $C_6H_4C(CH_3)_3$), 7.71-7.75 (m, 2H, C_5H_5N), 7.91 (d, *J* = 7.8 Hz, 2H, $C_6H_4C(CH_3)_3$), 8.92 (d, *J* = 8.0 Hz, 2H, C_5H_5N). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ = 20.8 (FcCH*C*H_3), 31.3 ($C_6H_4C(CH_3)_3$), 57.0 (Fc*C*HCH$_3$), 65.8 (Fc-*C*), 67.8 (Fc-*C*), 69.1 (Fc-*C*), 70.1 (Fc-*C*), 87.1 (Fc-*C*), 118.7 (N*C*HCHN), 123.3 (NCH*C*HN), 124.4 (C_5H_5N), 125.3 ($C_6H_4C(CH_3)_3$), 126.2 ($C_6H_4C(CH_3)_3$), 137.9 (C_5H_5N), 147.4 ($C_6H_4C(CH_3)_3$), 151.3 (C_5H_5N), 151.4 ($C_6H_4C(CH_3)_3$), 153.3 (Pd-$C_{carbene}$).

3c: Yield: 66% (0.29 g). m.p.: 160-161 °C. *Anal*. Calc. for $C_{27}H_{27}Cl_2FeN_3OPd$ (MW = 642.69 g.mol^{-1}): C, 50.46; H, 4.23; N, 6.54. Found: C, 50.33; H, 4.16; N, 6.76%. ^{1}H NMR (400 MHz,

$CDCl_3$, TMS, ppm): δ = 1.21 (s, 3H, FcCHCH_3), 3.80 (s, 3H, C_6H_4-*p*-(OCH_3)), 4.07 (s, 5H, Fc-*H*), 4.12 (s, 2H, Fc-*H*), 4.22 (s, 1H, Fc-*H*), 4.39 (s, 1H, Fc-*H*), 6.97 (d, *J* = 2.0 Hz, 2H, NC*H*C*H*N), 7.05-7.08 (m, 1H, FcC*H*CH_3), 7.25-7.27 (m, 1H, C_6H_4(OCH_3), 7.30-7.35 (m, 2H, C_5H_5H, 1H, C_6H_4(OCH_3)), 7.54 (m, 1H, C_6H_4(OCH_3), 7.78 (t, *J* = 7.6 Hz, 1H, C_5H_5N), 8.27-8.29 (m, 1H, C_6H_4(OCH_3), 8.82 (d, *J* = 4.0 Hz, 2H, C_5H_5N).^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ = 28.9 (FcCH*C*H_3), 55.5 (Fc*C*HCH_3), 68.8 (C_6H_4-p-(O*C*H_3)), 78.5 (Fc-*C*), 78.8 (Fc-*C*), 79.0 (Fc-*C*), 79.2 (Fc-*C*), 93.2 (Fc-*C*), 114.8 (*C*$_6H_4$(CH_3)), 122.7 (N*C*HCHN), 125.3 (NCH*C*HN), 127.4 (*C*$_6H_4$(CH_3)), 127.6 (*C*$_6H_4$(CH_3)), 127.8 (*C*$_6H_4$(CH_3)), 128.9 (*C*$_6H_4$(CH_3)), 129.6 (*C*$_5H_5$N), 137.2 (*C*$_5H_5$N), 152.9 (*C*$_5H_5$N), 158.9 (Pd-$C_{carbene}$).

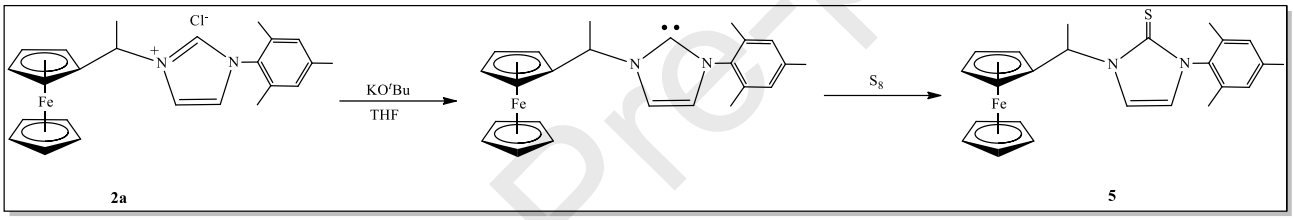
4: Yield: 44% (0.24 g). m.p.: 165-166 ^{o}C. *Anal*. Calc. for $C_{36}H_{40}Cl_2FeN_4Pd$ (MW = 761.90 g.mol^{-1}): C, 56.75; H, 5.29; N, 7.35. Found: C, 56.85; H, 5.46; N, 7.43%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ = 1.95 (s, 6H, C_6H_2(CH_3)$_3$-*p*-(CH_3)), 1.98 (d, *J* = 6.7 Hz, 3H, FcCHCH_3), 2.21 (s, 3H, C_6H_2(CH_3)$_3$-*o*-(CH_3)), 2.26 (s, 3H, C_6H_2(CH_3)$_3$-*p*-(CH_3)), 2.29 (s, 3H, C_6H_2(CH_3)$_3$-*o*-(CH_3)), 2.33 (s, 3H, C_6H_2(CH_3)$_3$-*o*-(CH_3)), 4.19 (s, 2H, Fc-*H*), 4.26 (s, 5H, Fc-*H*), 4.40 (s, 1H, Fc-*H*), 4.75 (s, 1H, Fc-*H*), 6.72 (d, *J* = 4.0 Hz, 1H, NC*H*CHN), 6.86 (d, *J* = 4.0 Hz, 1H, NCHC*H*N), 6.90 (s, 2H, C_6H_2(CH_3)$_3$), 6.95 (s, 1H, NC*H*CHN), 6.98 (s, 2H, C_6H_2(CH_3)$_3$), 7.14-7.18 (m, 1H, FcC*H*CH_3), 7.66 (s, 1H, NCHC*H*N), 8.03 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ = 15.4 (FcCH*C*H_3), 18.6 (C_6H_2(CH_3)$_3$-*o*-(*C*H_3)), 18.7 (C_6H_2(CH_3)$_3$-*o*-(*C*H_3)), 20.7 (C_6H_2(CH_3)$_3$-*p*-(*C*H_3)), 21.2 (C_6H_2(CH_3)$_3$-*p*-(*C*H_3)), 51.36 (FcC*H*CH_3), 66.0 (Fc-*C*), 67.8 (Fc-*C*), 69.5 (Fc-*C*), 70.1 (Fc-*C*), 87.6 (Fc-*C*), 116.8 (N*C*HCHN), 119.8 (N*C*HCHN), 122.8 (N*C*HCHN), 125.2 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 131.3 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 134.1 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 135.7 (NCH*C*HN), 136.5 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 137.2 (Fc-*C*CHCH$_3$N), 139.1 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 140.1 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 140.4 (NC*H*N), 144.4 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 145.0 (*C*$_6H_2$(CH_3)$_3$-*o*-(CH_3)), 154.1 (Pd-*C*$_{carbene}$).

2.3. Preparation of the N-ferrocenylethyl-N'-(2,4,6-trimethylphenyl)imidazole-2-thione, ***5***.

A Schlenk flask was charged with imidazolium salt (**3a**, 1.0 mmol), K^{t}OBu (1.4 mmol), and 15 mL dry THF. After this mixture was stirred at 25 ^{0}C for one hour, S_8 (2.0 mmol) was added (Scheme 3). After two hours, H_2O (10.0 mL) was added to the reaction mixture, and the organic phase was extracted with Et_2O (10.0 mLx2). Subsequently, the organic phase was dried with

$MgSO_4$. The Et_2O phase was concentrated in vacuum and the product precipitated by addition of hexane.

Yield: 40% (0.172 g). m.p.: 137-138 °C. *Anal*. Calc. for $C_{24}H_{26}FeN_2S$ (MW = 430.38 g.mol^{-1}): C, 66.98; H, 6.09; N, 6.51. Found: C, 66.86; H, 6.03; N, 6.75%. ^{1}H NMR (400 MHz, DMSO-d_6, TMS, ppm): δ = 1.67 (d, J = 7.0 Hz, 3H, FcCHCH_3), 1.90 (d, J = 8.0 Hz, 6H, $C_6H_2(CH_3)_3$-*o*-(CH_3)), 2.27 (s, 3H, $C_6H_2(CH_3)_3$-*p*-(CH_3)), 4.14-4.16 (m, 1H, Fc-*H*), 4.18-4.19 (m, 1H, Fc-*H*), 4.21 (s, 5H, Fc-*H*), 4.26 (s, 1H, Fc-*H*), 4.36 (s, 1H, Fc-*H*), 5.91 (q, J = 4.0 Hz, 1H, FcC*H*CH_3), 6.96 (s, 2H, $C_6H_2(CH_3)_3$), 7.15 (s, 2H, NC*H*C*H*N). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ = 17.4 (FcCH*C*H_3, $C_6H_2(CH_3)_3$-*o*-(*C*H_3)), 19.7 ($C_6H_2(CH_3)_3$-*o*-(*C*H_3)), 20.5 ($C_6H_2(CH_3)_3$-*p*-(*C*H_3)), 66.2 (Fc*C*HCH$_3$), 68.6 (Fc-*C*), 78.5 (Fc-*C*), 78.9 (Fc-*C*), 79.1 (Fc-*C*), 79.2 (Fc-*C*), 88.9 (Fc-*C*), 127.4 (N*C*HCHN), 127.6 (NCH*C*HN), 127.9 ($C_6H_2(CH_3)_3$), 128.5 ($C_6H_2(CH_3)_3$), 133.9 ($C_6H_2(CH_3)_3$), 135.2 ($C_6H_2(CH_3)_3$), 135.3 ($C_6H_2(CH_3)_3$), 137.9 ($C_6H_2(CH_3)_3$), 160.9 ($C_{carbene}$-S).



Scheme 3. Synthesis of *N-ferrocenylethyl-N'-(2,4,6-trimethylphenyl)imidazole-2-thione*, **5**.

2.4. X-ray crystallography

Intensity data of the compounds were collected on a STOE IPDS II diffractometer at room temperature using graphite-monochromated Mo Kα radiation by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA [19] while data reduction was applied using X-RED32 [19]. The structure was solved by direct methods using SHELXS-2013 [20] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2014 [21] implemented in WinGX [22] program suit. All carbon bound H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.93, 0.98 and 0.96 Å for aromatic CH, methine CH and CH_3 atoms, respectively. The displacement parameters of the H atoms were fixed at U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for CH_3) of their parent atoms. Crystal data, data collection and structure refinement details are summarized in Table 1 while important bond

lengths and angles are collected in Table 2. PLATON [23] was used for the structure analysis. Molecular graphics were generated by using ORTEP-3 [22].

Table 1. Crystal data and structure refinement parameters for **4** and **5**.

Parameter	**4**	**5**
CCDC depository	1472057	1472056
Color/shape	Yellow/plate	Yellow/plate
Chemical formula	$[FePdCl_2(C_5H_5)(C_{19}H_{21}N_2)(C_{12}H_{14}N_2)]$	$[Fe(C_5H_5)(C_{19}H_{21}N_2S)]$
Formula weight	761.87	430.38
Temperature (K)	296	296
Wavelength (Å)	0.71073 Mo Kα	0.71073 Mo Kα
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Unit cell parameters		
a, b, c (Å)	19.6604(11), 8.7608(3), 20.8479(11)	7.3883(5), 12.1643(8), 13.4322(9)
α, β, γ (°)	90, 100.266(4), 90	63.974(5), 74.630(5), 78.015(4)
Volume (Å^3)	3533.4(3)	1040.16(13)
Z	4	2
D_{calc} (g/cm^3)	1.432	1.374
μ (mm^{-1})	1.101	0.837
Absorption correction	Integration	Integration
T_{min}, T_{max}	0.6943, 0.9487	0.6592, 0.9741
F_{000}	1560	452
Crystal size (mm^3)	0.53 × 0.17 × 0.07	0.58 × 0.22 × 0.04
Diffractometer/measurement method	STOE IPDS II/ω scan	STOE IPDS II/ω scan
Index ranges	$-23 \le h \le 22$, $-10 \le k \le 10$, $-24 \le l \le 24$	$-9 \le h \le 9$, $-16 \le k \le 16$, $-17 \le l \le 17$
θ range for data collection (°)	$1.985 \le \theta \le 25.247$	$1.721 \le \theta \le 28.419$
Reflections collected	22832	18785
Independent/observed reflections	6408/2564	5203/3809
R_{int}	0.1278	0.100
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6408/0/403	5203/0/257
Goodness-of-fit on F^2	0.804	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0524$, $wR_2 = 0.0637$	$R_1 = 0.0426$, $wR_2 = 0.0887$
R indices (all data)	$R_1 = 0.1663$, $wR_2 = 0.0825$	$R_1 = 0.0685$, $wR_2 = 0.0968$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.347, −0.318	0.310, −0.295

Table 2. Selected geometric parameters for **4** and **5**.

Parameter	4	Parameter	5
Bond lengths (Å)			
S1─C10	*2.3021(19)*	*Pd1─Cl1*	*1.685(2)*
N1─C6	*2.3021(19)*	*Pd1─Cl2*	*1.432(3)*
N1─C10	*2.068(5)*	*Pd1─N2*	*1.361(3)*
N1─C11	*1.949(7)*	*Pd1─C24*	*1.393(3)*
N2─C10	*1.445(8)*	*N1─C1*	*1.364(3)*
N2─C12	*1.350(7)*	*N1─C10*	*1.389(3)*
N2─C13	*1.368(7)*	*N1─C12*	*1.468(3)*
C11─C12	*1.318(7)*	*N2─C10*	*1.331(4)*
	1.361(7)	*N2─C11*	
	1.375(8)	*N3─C22*	
	1.377(7)	*N3─C24*	
	1.442(8)	*N3─C13*	
	1.339(8)	*N4─C24*	
	1.376(8)	*N4─C23*	
	1.481(8)	*N4─C25*	
	1.345(8)	*C11─C12*	
	1.306(10)	*C22─C23*	
Bond angles (°)			
N1─C10─S1	*175.8(3)*	*C24─Pd1─N2*	*126.66 (15)*
N2─C10─S1	*88.72(19)*	*C24─Pd1─Cl1*	*127.87 (17)*
N1─C10─N2	*90.27(16)*	*N2─Pd1─Cl1*	*105.46 (17)*
C12─C11─N1	*89.81(19)*	*C24─Pd1─Cl2*	*107.3 (2)*
C10─N1─C11	*91.06(17)*	*N2─Pd1─Cl2*	*109.83 (18)*
C10─N1─C6	*177.49(9)*	*Cl1─Pd1─Cl2*	*124.97 (17)*
C11─N1─C6	*112.9(6)*	*N2─C10─N1*	*125.14 (19)*
C11─C12─N2	*104.2(6)*	*N4─C24─N3*	*107.72 (19)*
C10─N2─C12	*105.1(6)*	*C10─N1─C12*	*109.66 (19)*
C10─N2─C13	*127.8(6)*	*C10─N1─C1*	*123.96 (18)*
C12─N2─C13	*126.9(6)*	*C12─N1─C1*	*126.32 (18)*
	104.4(6)	*C10─N2─C11*	
	108.6(6)	*C22─N3─C24*	
	125.4(6)	*C22─N3─C13*	
	126.0(6)	*C24─N3─C13*	
	111.7(6)	*C24─N4─C23*	
	125.0(6)	*C24─N4─C25*	
	123.3(7)	*C23─N4─C25*	
	107.2(6)	*C11─C12─N1*	
	110.4(7)	*C12─C11─N2*	
	109.2(7)	*C23─C22─N3*	
	106.2(8)	*C22─C23─N4*	

Table 3. Hydrogen bonding geometry for **4** and **5.**

D—H···A	D—H (Å)	H···A (Å)	D···A (Å)	D—H···A (°)
4				
C19─H19A···Cl1	0.96	2.70	3.656(9)	176
C21─H21A···Cl2	0.96	2.74	3.631(8)	154
C10─H10···Cl1	0.93	2.65	3.163(7)	115
C12─H12···Cl1^{i}	0.93	2.72	3.642(7)	170
5				
C13─H13···S1	0.98	2.68	3.220(2)	115

Symmetry code: ^{i} *x*, *y*+1, *z*.

3. Results and discussion

3.1. Synthesis of ferrocenyl imidazolium salts (2a-c)

The ferrocenyl imidazolium salts can be efficiency synthesized starting from ferrocene according to the literature method [3a,24] (Scheme 1). The reduction of acetylferrocene prepared by Friedel-Crafts acylation reaction of ferrocene gave 1-ferrocenylethanol in excellent yield. Treatment of 1-ferrocenylethanol with 1-substituted imidazole in acetic acid at 60 ^{0}C for 7 h gave an imidazolium salt with the acetate as a counter anion. Subsequently, addition of excess LiCl to the reaction mixture resulted in anion exchange to give ferrocenyl imidazolium chlorides. The new compounds were characterized by their spectroscopic data and elemental analyses. The ^{1}H NMR signals of the C(2)-*H* protons were observed as sharp singlets at chemical shifts of 9.87, 10.24, and 10.05 and ppm for **2a-c** ligands, respectively. In the ^{13}C-NMR spectra of **2a-c**, the characteristic signals of the imino carbon (N*C*HN) were detected as typical singlets at 140.0, 152.4, and 159.8 ppm, respectively.

*3.2. Synthesis of ferrocenyl-NHC palladium complexes (**3b**,**3c**,**4**)*

The synthesis of ferrocenyl NHC-palladium complexes (**3b**,**3c**,**4**) is achieved by refluxing of the corresponding imidazolium salt **2a–c**, with palladium chloride (1.0 eq.) in presence of K_2CO_3 in pyridine in an argon atmosphere, as shown in Scheme 2. All of these palladium complexes are air and moisture stable and can be stored under air in solid-state without any decomposition. This complex **4** was fully characterized by NMR spectroscopy, elemental analyses, and X-ray diffraction method. The proton signal of NC*H*N from the imidazolium chlorides at ca. 9–10 ppm was absent in the ^{1}H NMR of palladium complexes, confirming carbene generation. In addition,

the formation of the metal complexes was evident from the distinctive Pd–$C_{carbene}$ peak 150–160 ppm.

The general method for the preparation of PEPPSI-type Pd(II)-NHC complexes by reacting $PdCl_2$ with imidazolium salts in the presence of excess K_2CO_3 worked well for **3b** and **3c** derivatives. However, the reaction of the sterically hindered N-mesitylene substituted imidazolium salt **2a** under similar reaction conditions gave the N-coordinated mesityl-imidazole ligand, which presumably resulted from N-C cleavage of the N-mesityl group under these reaction conditions [25]. We do not have any data at this stage on whether there is such a situation in other substituents. It is understood that the main product in the synthesis of PEPPSI-type Pd complexes of 4-*tert*-butyl- and 4-methoxyphenyl substituted imidazolium salts are complexes of type [$PdCl_2$ (NHC)py], **3b**,**c**.

*3.3. Synthesis of N-ferrocenylethyl-N'-(2,4,6-trimethylphenyl)imidazole-2-thione (**5**)*

N-ferrocenylethyl-N'-(2,4,6-trimethylphenyl)imidazole-2-thione **5** was synthesized via the reaction of the corresponding imidazolium salt **2a** with potassium *tert*-butoxite and elemental sulphur in tetrahydrofuran in moderate yield. The ($C_{carbene}$-S) resonance of this complex in the ^{13}C NMR spectra appeared at 160.9 ppm.

3.4. Description of crystal structures

The structures of compounds **4** and **5** were unambiguously determined by single-crystal X-ray diffraction. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell, and is shown in Fig. 1. The central palladium atom is tetracoordinated with one carbene carbon atom, one imidazole nitrogen atom and two chlorine atoms to adopt a slightly distorted *trans*-square-planar geometry. In the square-planar coordination, atoms Pd1, Cl1, Cl2, N2 and C24 deviate by 0.0454(6), 0.004(2), 0.004(2), −0.026(6) and −0.027(8) Å, respectively, from the mean plane through these five atoms. The Pd─N and Pd─C distances are 2.068(5) and 1.949(7) Å, respectively, comparable to those in other palladium(II)-NHC analogues [26,27]. The Cl1─Pd1─Cl2 and C24─Pd1─N2 arrays are almost linear with the bond angles of 177.49(9) and 175.8(3)°, respectively. The angle sum about the divalent Pd atom is 359.86°, the greatest deviation from orthogonality being 88.72(19)° for C24─Pd1─Cl1. As shown in Fig. 1, the

$PdCNCl_2$ coordination plane is almost oriented perpendicularly to the N3/N4/C22-24 ring plane with a dihedral angle of 76.8(4)°, and is twisted from the N1/N2/C10-12 ring plane by 20.9(4)°.

The Fe─C distances are as expected for a ferrocene derivative, changing from 1.975(10) to 2.038(11) Å. The cyclopentadienyl (Cp) rings are roughly eclipsed, with a twist angle τ = 6.3(14)°, and they are slightly tilted with respect to each other, forming a dihedral angle of 1.8(8)°. The Fe-to-centroid distances are 1.6313(12) Å (*Cg*3) and 1.6374(12) Å (*Cg*4), and the *Cg*3─Fe1─*Cg*4 angle is 179.06(8)° (*Cg*3 and *Cg*4 are the centroids of the C27-C31 and C32-C36 rings, respectively).

In the molecular structure of **4**, intramolecular C19─H19A···Cl1, C21─H21A···Cl2 and C10─H10···Cl1 contacts lead to the formation of eight- and five-membered rings with graph-set descriptor *S*(8) for the first two, and *S*(5) for the last one [28]. In the crystal structure, atom C12 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to the Cl1 atom in the molecule at (*x*, *y*+1, *z*), forming a *C*(6) [27] chain running parallel to the *b* axis (Fig. 2).

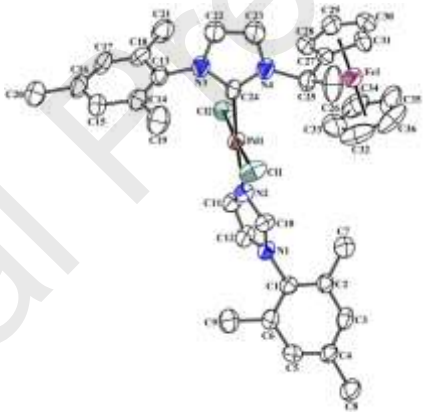


Figure 1. A view of **4** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for the sake of clarity.

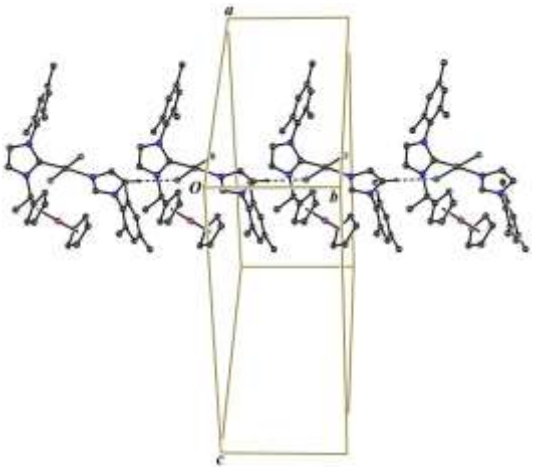


Figure 2. Part of the crystal structure of **4**, showing a *C*(6) chain along [010]. For the sake of clarity, H atoms not involved in H-bonds have been omitted.

Compound **5** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell, and is shown in Fig. 3. The C═S bond length of 1.685(2) Å is intermediate between the single-bond value of 1.81 Å and the double-bond value of 1.61 Å [29]. The shortening of the two adjacent N1─C10 and N2─C10 bonds also confirms the existence of some partial double-bond character [1.361(3) and 1.364(3) Å]. The bond angle sums about N1 and N2 both sum to 359.94°, indicating sp^2 hybridization. The C11─C12 bond length of 1.331(4) Å in the five-membered imidazole ring (sum of pentagonal internal angles ≅ 540.0°) is the same with the average for a non-delocalized olefinic C═C grouping (1.331 Å) [30]. These data show that the major contributors to the resonance hybrid for **5** mainly involve the electrons of N1, N2, C10 and S1 atoms, and this is a normal feature for the thiourea systems [3a, 31-34].

The Fe─C distances fall within the expected range, ranging from 2.035(3) to 2.049(3) Å, which agree well with those reported for ferrocene derivatives [35-37]. Similar to **4**, the Cp rings are roughly eclipsed, with a twist angle τ = 8.0(2)°, and they are slightly tilted with respect to each other, forming a dihedral angle of 1.4(2)°. The Fe-to-centroid distances are 1.6434(4) Å (*Cg*1) and 1.6527(4) Å (*Cg*2), and the *Cg*1─Fe1─*Cg*2 angle is 178.82(3)° (*Cg*1 and *Cg*2 are the centroids of the C15-C19 and C20-C24 rings, respectively).

In the molecular structure of **5**, a weak intramolecular contact between the methine H and sulphur atoms leads to the formation of a five-membered ring with graph-set descriptor *S*(5) [28]. In the crystal structure, there are no important interactions between the molecules, other than van

der Waals contacts. Full details of the hydrogen-bonding geometries in **4** and **5** are given in Table 3.

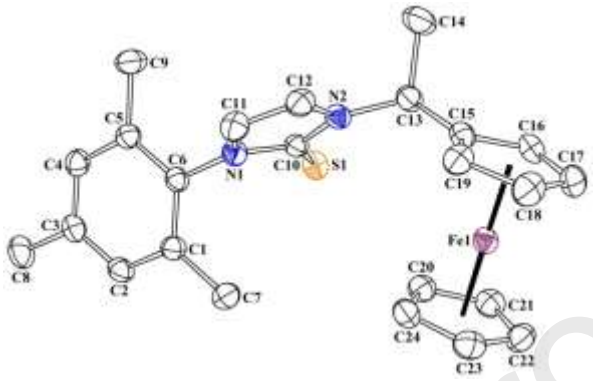


Figure 3. A view of **5** showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for the sake of clarity.

4. Conclusions

In this study, ferrocenyl-substituted novel PEPPSI-type Pd(II)-NHC complexes (**3a**,**b**), mesityl-imidazole bearing Pd(II)-NHC complex (**4**), and thione derivative (**5**) have been prepared. All synthesized complexes have been characterized by ^{1}H- and ^{13}C-NMR, and elemental analyses. In addition, the structures of synthesized compounds **4** and **5** were described by the X-ray diffraction analysis method. The syntheses of Pd(II)-NHC complexes were performed at the presence of excess K_2CO_3 which was necessary to detach proton at C2 of imidazolium salts. In these reaction conditions, it is seen that the C-N bond in the imidazolium salt (**2a**) is cleavage, and a compound of **4** is formed.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was financially supported by the Scientific Research Unit (BAP, project number: FEF-13021) of Aydın Adnan Menderes University and Ondokuz Mayıs University (Project No: PYO.FEN.1906.19.001).

Appendix A. Supplementary data

CCDC 1472056 and 1472057 contain the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/].

References

[1] a) A.A. Danopoulos, T. Simler, P. Braunstein. Chem. Rev. 119 (2019) 3730-3961. https://doi.org/10.1021/acs.chemrev.8b00505,

b) O. Kìhl, Functionalised N-Heterocyclic Carbene Complexes, Wiley-VCH, Weinheim, 2010,

c) S. Diez-Gonzalez, N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools, Royal Society of Chemistry, Cambridge, 2011,

d) S. P. Nolan, N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis, Wiley-VCH, Weinheim, 2014,

e) M.N. Hopkinson, C. Richter, M. Schedler, F.Glorius. Nature 510 (2014) 485-496. https://doi:10.1038/nature13384,

[2] a) F.E. Hahn, M. C. Jahnke. Angew. Chem., Int. Ed. 47 (2008) 3122-3172. https://doi.org/10.1002/anie.200703883,

b) F.E. Hahn. Angew. Chem., Int. Ed. 45 (2006) 1348-1352. https://doi.org/10.1002/anie.200503858,

c) K.J. Cavell, D.S. McGuinnes. Coord. Chem. Rev. 248 (2004) 671-681. https://doi.org/10.1016/j.ccr.2004.02.006,

d) V. César, S. Bellemin-Laponnaz, L.H. Gade. Chem. Soc. Rev. 33 (2004) 619-636. https://doi.org/10.1039/B406802P,

e) C.M. Crudden, D.P. Allen. Coord. Chem. Rev. 248 (2004) 2247-2273. https://doi.org/10.1016/j.ccr.2004.05.013,

f) W.A. Herrmann. Angew. Chem., Int. Ed. 41 (2002) 1290-1309. https://doi.org/10.1002/1521-3773(20020415)41:8<1290::AID-ANIE1290>3.0.CO;2-Y,

g) W.A. Herrmann, T. Weskamp, V.P.W. Böhm. Adv. Organomet. Chem. 48 (2001) 1-69. https://doi.org/10.1016/S0065-3055(01)48001-4,

h) A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan. J. Organomet. Chem. 653 (2002) 69-82. https://doi.org/10.1016/S0022-328X(02)01154-3,

i) D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand. Chem. Rev. 100 (2000) 39-92. https://doi.org/10.1021/cr940472u,

j) W.A. Herrmann, C. Köcher. Angew. Chem., Int. Ed. 36 (1997) 2162-2187. https://doi.org/10.1002/anie.199721621,

[3] a) H. Seo, B.Y. Kim, J.H. Lee, H.-J. Park, S.U. Son, Y.K. Chung. Organometallics 22 (2003) 4783-4791. https://doi.org/10.1021/om0303193,

b) A. Bertogg, F. Camponovo, A. Togni. Eur. J. Inorg. Chem. (2005) 347-356. https://doi.org/10.1002/ejic.200400691,

c) H.A. Özbek, P.S. Aktaş, J.-C. Daran, M. Oskay, F. Demirhan, B. Çetinkaya. Inorg. Chim. Acta 423 (2014) 435-442. https://doi.org/10.1016/j.ica.2014.08.036,

[4] a) C.D. Varnado, V.M. Lynch, C.W. Bielawski. Dalton Trans. (2009) 7253-7261. https://doi.org/10.1039/B908696J,

b) D. Onyancha, C. McCleland, T. Gerber. Chem. Sci. J. 7 (2016) 117-122. http://dx.doi.org/10.4172/2150-3494.1000117,

[5] P. He, Y. Du, S. Wang, C. Cao, X. Wang, G. Pang, Y. Shi. Z. Anorg. Allg. Chem. 639 (2013) 1004-1010. https://doi.org/10.1002/zaac.201300097,

[6] B. Bildstein, M. Malaun, H. Kopacka, K. Wurst, M. Mitterböck, K.-H. Ongania, G. Opromolla, P. Zanello. Organometallics 18 (1999) 4325-4336. https://doi.org/10.1021/om990377h,

[7] B. Bildstein, M. Malaun, H. Kopacka, K.-H. Ongania, K. Wurst. J. Organomet. Chem. 572 (1999) 177-187. https://doi.org/10.1016/S0022-328X(98)00943-7,

[8] B. Bildstein, M. Malaun, H. Kopacka, K.-H. Ongania, K. Wurst. J. Organomet. Chem. 552 (1998) 45-61. https://doi.org/10.1016/S0022-328X(97)00464-6,

[9] K.S. Coleman, S. Turberville, S.I. Pascu, M.L.H. Green. J. Organomet. Chem. 690 (2005) 653-658. https://doi.org/10.1016/j.jorganchem.2004.10.019,

[10] D.M. Khramov, E.L. Rosen, V.M. Lynch, C.W. Bielawski. Angew. Chem., Int. Ed. 47 (2008) 2267-2270. 10.1002/anie.200704978,

[11] U. Siemeling, C. Färber, C. Bruhn. Chem. Commun. (2009) 98-100. https://doi.org/10.1039/B813809E,

[12] U. Siemeling, C. Färber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedeckec, G. Frenking. Chem. Sci. 1 (2010) 697-704. https://doi.org/10.1039/C0SC00451K,

[13] S. Gischig, A. Togni. Organometallics 24 (2005) 203-205. https://doi.org/10.1021/om049097e,

[14] Z. Jin, Y. Hu, A. Huo, W. Tao, L. Shao, J. Liu, J. Fang. J. Organomet. Chem. 691 (2006) 2340–2345. https://doi.org/10.1016/j.jorganchem.2005.11.029,

[15] B. Yenisarı, MSc Thesis, Graduate School of Natural Sciences-Aydın Adnan Menderes University, 2014,

[16] A.W. Van der Made, R.H. Van der Made. J. Org. Chem. 58 (1993) 1262-1263. https://doi.org/10.1021/jo00057a046,

[17] X. Zeng, X. Yang, Y. Zhang, C. Qing, H. Zhang. Bioorg. Med. Chem. Lett. 20 (2010) 1844-1847. https://doi.org/10.1016/j.bmcl.2010.01.163,

[18] E.P. Çoban, R. Fırıncı, H. Biyik, M.E. Günay, Braz. J. Pharm. Sci. 53 (2017) e15075-e15085. http://dx.doi.org/10.1590/s2175-97902017000115075.

[19] Stoe & Cie, X-AREA Version 1.18 and X-RED32 Version 1.04, Stoe & Cie, Darmstadt, Germany, 2002,

[20] G.M. Sheldrick. Acta Crystallogr. A 64 (2008) 112-122. https://doi.org/10.1107/S0108767307043930,

[21] G.M. Sheldrick. Acta Crystallogr. C 71 (2015) 3-8. https://doi.org/10.1107/S2053229614024218,

[22] L.J. Farrugia. J. Appl. Crystallogr. 45 (2012) 849-854. https://doi.org/10.1107/S0021889812029111,

[23] A.L. Spek. Acta Crystallogr. C 71 (2015) 9-18. https://doi.org/10.1107/S2053229614024929,

[24] L. Bechki, T. Lanez. Asian J. Chem. 22 (2010) 5523-5527. WOS:000279844800082,

[25] a) X.-B. Shen, T.-T. Gao, J.-M. Lu, L.-X. Shao. J Organometal. Chem. 25 (2011) 497-501. https://doi.org/ 10.1002/aoc.1792

b) H. V. Huynh, J. Wu. J. Organomet. Chem. 694 (2009) 323-331. https://doi.org/10.1016/j.jorganchem.2008.10.044,

[26] Z.-Y. Wang, G.-Q. Chen, L.-X. Shao. J. Org. Chem. 77 (2012) 6608-6614. https://doi.org/10.1021/jo301270t,

[27] P. Huang, Y.-X. Wang, H.-F. Yu, J.-M. Lu. Organometallics 33 (2014) 1587-1593. https://doi.org/10.1021/om401028d,

[28] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang. Angew. Chem., Int. Ed. Engl. 34 (1995) 1555-1573. https://doi.org/10.1002/anie.199515551,

[29] K.P. Bhabak, K. Satheeshkumar, S. Jayavelu, G. Mugesh. Org. Biomol. Chem. 9 (2011) 7343-7350. https://doi.org/10.1039/c1ob05773a,

[30] C. Williamson, J.M.D. Storey, W.T.A. Harrison. J. Chem. Crystallogr. 36 (2006) 277-282. https://doi.org/10.1007/s10870-005-9032-x,

[31] Y. Yokomori, O. Moriya, Y. Urata. Anal. Sci. 6 (1990) 791-792. https://doi.org/10.2116/analsci.6.791,

[32] M.K. Denk, S. Gupta, J. Brownie, S. Tajammul, A.J. Lough. Chem. Eur. J. 7 (2001) 4477-4486.https://doi.org/10.1002/1521-3765(20011015)7:20<4477::AID-CHEM4477>3.0.CO;2-I,

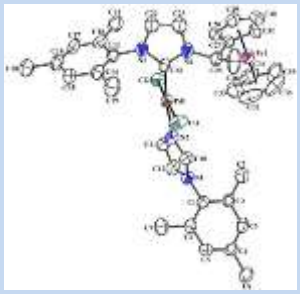
[33] C. Marshall, M.F. Ward, W.T.A. Harrison. J. Organomet. Chem. 690 (2005) 3970-3975. https://doi.org/10.1016/j.jorganchem.2005.05.036,

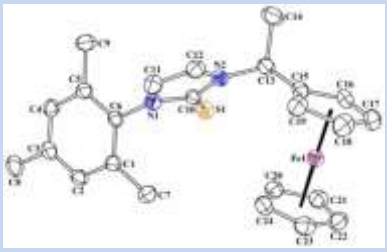
[34] H. Zhu, Q. Ma, A.-Q. Jia, Q. Chen, W.-H. Leung, Q.-F. Zhang. Inorg. Chim. Acta. 405 (2013) 427-436. https://doi.org/10.1016/j.ica.2013.06.033,

[35] N.M. Toma, J.-C. Daran, H. Merazig, E. Manoury. Acta Crystallogr. C 70 (2014) 460-464. https://doi.org/10.1107/S2053229614007554,

[36] N.G. Shikhaliyev, A.V. Gurbanov, V.M. Muzalevsky, V.G. Nenajdenko, V.N. Khrustalev, Acta Crystallogr. E 70 (2014) m286-m287. https://doi.org/10.1107/S1600536814014366,

[37] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang. Angew. Chem., Int. Ed. Engl. 34 (1995) 1555−1573. https://doi.org/10.1002/anie.199515551.





Highlights

- The ferrocenyl-functionalized N-heterocyclic carbene (NHCs) precursors were synthesized.
- The novel ferrocenyl-bearing PEPPSI-type palladium complexes were synthesized.
- Imidazole-2-thione derivative was synthesized via the deprotonation method.
- The excess base play a role in cleavage the C-N bond in the imidazole salt.

Author Statement

Betil Yenisarı: Investigation, MSc. Student.

Rukiye Fırıncı: Investigation, visualization.

Namık Özdemir: Software, X-ray analysis.

M. Emin Günay: Supervision, writing-reviewing and editing,